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# CORROSION AND CORROSION PROTECTION OF STEEL IN CONCRETE

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## FEATURES OF THE MECHANISM OF RE-ALKALISATION AND DESALINATION TREATMENTS FOR REINFORCED CONCRETE

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### ABSTRACT

Re-alkalisation and desalination are electrochemical techniques which are becoming increasingly popular alternatives to mechanical repair as a means of rehabilitating corrosion damaged reinforced concrete. They both involve applying a low voltage direct current between the reinforcing steel and an external electrode. In desalination (also known as chloride extraction or chloride removal) chloride ions migrate out of the concrete towards the anode, where they dissolve in water held against the surface. In re-alkalisation a sodium carbonate solution is held against the surface and is claimed to migrate into the concrete, raising its pH. Of the various mechanisms which could contribute, simple concentration-gradient-controlled diffusion of the species through concrete is too slow to be significant. Electromigration under the influence of the applied field is probably the main contributor in desalination but it cannot allow sodium carbonate to penetrate in re-alkalisation and a combination of electro-osmosis and direct absorption are probably the main contributors here.

**Keywords:** Concrete repair, electrochemical treatment, desalination, re-alkalisation, chlorides, corrosion, electromigration, diffusion, electro-osmosis, pH, sodium carbonate, mechanisms.

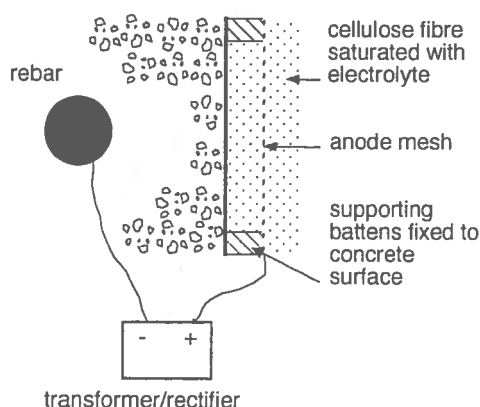
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## INTRODUCTION

Re-alkalisation and desalination are electrochemical techniques which are becoming increasingly popular alternatives to mechanical repair as a means of rehabilitating corrosion damaged reinforced concrete. There are different opinions about their action and this paper is an attempt to clarify some of the issues. It aims to identify the principal participants in the overall processes, to explore their physical chemical basis and make a preliminary assessment of their likely contribution.

## OUTLINE OF THE TREATMENTS

Referring to Fig. 1, the re-alkalisation and desalination treatments are broadly similar. Steel or inert titanium mesh anodes are held against the surface of the concrete to be treated and surrounded by electrolyte. The anodes are connected through a transformer/rectifier to the embedded steel reinforcement in a few places to make the electrical connections and produce the cathode. The reinforcement is covered over again to prevent short circuits. In re-alkalisation currents of up to  $1 \text{ A/m}^2$  are applied for between three and seven days with sodium carbonate as the electrolyte. At the end of this time alkalinity has been restored to the concrete around the reinforcing bar and between it and the surface. The pH of 10.5 conferred by sodium carbonate is assumed to be high enough to repassivate the steel and prevent corrosion, but long term evidence is not yet available to confirm this. In desalination the same current density is applied for longer periods of five to eight weeks and the chloride ion concentration within the concrete between the surface and the embedded bar is reduced. The total charge passed is  $100\text{--}200 \text{ Ah/m}^2$  in re-alkalisation and about  $1500 \text{ Ah/m}^2$  in desalination. There is some indication that an interrupted treatment removes more chloride ion than a continuous treatment. Both treatments can be controlled and monitored effectively by microcomputer [1].



The main and desirable consequences of the treatments are a rise in pH around the reinforcing bar and a reduction in chloride ion concentration. Disadvantages, which are the subject of research in various countries, are possible reductions in bond strength, possible increased risk of alkali-aggregate reaction resulting from higher sodium and potassium concentrations in the concrete, and changes in the microstructure of the concrete which may modify mechanical and durability properties.

Fig. 1 Schematic diagram of a re-alkalisation or desalination treatment.

## ELECTROCHEMICAL PROCESSES

### Corrosion

The main features of the electrochemical corrosion of steel in concrete are well known and involve:



Thermodynamics dictates that at low pH the corrosion process is favoured but above pH 9 (the actual value depends on the external potential)  $\text{Fe}_2\text{O}_3$  is the favoured product and forms as a passive film of oxide on the surface of the steel to protect it against further corrosion. However, the protective passive film may be broken down by carbonation or in the presence of high concentrations of chloride ions.

In carbonation, atmospheric carbon dioxide dissolves in the pore solution and forms carbonic acid, which reacts with the calcium hydroxide to reduce the pH to below the level required for the steel to be passive.



Carbonation takes place most rapidly in conditions of intermediate humidity (50-70% relative humidity) because carbon dioxide cannot penetrate saturated concrete to react with calcium hydroxide, whereas in dry concrete there is insufficient water to dissolve it and form carbonic acid.

In contrast, chloride ion in the pore solution attacks and breaks down the passive oxide layer directly even though the pH is high enough for the steel to be passive. When added to the fresh mix, as a result of contaminated aggregate or mixing water or the deliberate use of admixtures, less than half of the total added chloride is found as free chloride in the pore water [2]. The rest is bound, and is probably present in the form of calcium chloroaluminate hydrate which may exist in equilibrium with the free chloride:



As with all chemical equilibria there are two consequences of this reaction. Firstly, the removal of free chloride ions by any process causes the chloroaluminate to dissociate, so that a low concentration measured at the end of a desalination process may rise with time as the equilibrium is slowly re-established. This may take days or weeks. Secondly, it is never possible to remove all the chloride with a single treatment, as was confirmed practically by Elsener et al [3]. Thirdly, chloride ions which are present as a result of migration into hardened concrete from an external source (e.g. deicing salt or seawater) take time to be bound as a result of the equilibrium reaction with the calcium aluminate hydrate and are likely to be more easily removed by desalination than chlorides which were cast into the original concrete. In addition, the rate of release may be affected by external factors and Tritthart et al [4] found that application of a direct current enhances the dissolution of bound chloride ion, possibly by local heating. This, in turn, can facilitate the desalination process.

### Treatment

Electrochemical treatments make the steel cathodic and generate hydroxyl ions (equation 2), strengthening the passive layer but, in addition, the more severe conditions in re-alkalisation and desalination mean that other electrochemical

processes may occur as follows:

(i) Water may be split into its constituents by the passage of electric current.

At the anode,  $2\text{H}_2\text{O} \rightarrow 2\text{O}_2 + 4\text{H}^+ + 4\text{e}^-$  [7]

At the cathode,  $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$  [8]

The production of hydroxyl ions around the cathode is helpful but the evolved hydrogen may be absorbed into the steel where it can cause embrittlement. In porous concrete it may simply diffuse harmlessly to atmosphere through the pores or along the concrete-steel interface. The reduction of water (equation 8) may account for the sometimes dry appearance of the steel when desalinated concrete is broken open for inspection. At the anode oxygen evolved will simply bubble out of the external treatment solution, but acid produced may etch the surface of the concrete.

(ii) Chloride ion may be oxidised to chlorine if the voltage is high enough:

$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$  [9]

This is a potential hazard because it will bubble out of the treatment solution to pose a health risk to site staff as the acceptable airborne concentration of chlorine is very low.

### MECHANISM OF THE TREATMENTS

There are three physical processes by which the penetration of alkaline electrolyte or extraction of chloride can happen:

(i) simple diffusion of ions and other dissolved species as a result of concentration gradients within the concrete;

(ii) electromigration of charged species as a result of the electric field between the cathodic reinforcing bars and the external anode;

(iii) bulk flow of external solution either by direct absorption or by electro-osmosis, where solution flows as a result of the electrical double layer on the walls of the pores taking any dissolved species with it.

### DIFFUSION

Fig. 2 summarises the diffusion processes which may take place during (a) re-alkalisation and (b) desalination treatment. In both cases diffusion is from a higher to a lower concentration and Fick's second law applies to the flux of species through the concrete:

$$-J(x) = \frac{dC(x)}{dt} = D_a \frac{d^2C}{dx^2} \quad [10]$$

where  $J(x)$  is the unidirectional flux ( $\text{mol/m}^2\text{s}$ ) of species  $j$  in the  $x$  direction with time  $t$ ,  $C(x)$  is its concentration ( $\text{mol/m}^3$ ) at point  $x$  and  $D_a$  is the apparent diffusion coefficient ( $\text{m}^2/\text{s}$ ). Andrade [5] formulates the solution to this as

$$C_x/C_s = 1 - \text{erf} \left\{ \frac{x}{2(D_a t)^{1/2}} \right\} \quad [11]$$

where  $C_s$  is the steady state concentration eventually reached at equilibrium.

Equation 11 may be used to calculate how long it would take to reach equilibrium by ionic diffusion if the following reasonable assumptions are made:

(i) There is steel 25mm below the free surface of the concrete, i.e.  $x = 0.025$ .

(ii) In re-alkalisation the mobile species are  $\text{Na}^+$  and  $\text{CO}_3^{2-}$  ions and in desalination they are  $\text{Na}^+$  and  $\text{Cl}^-$ .

(iii) The apparent diffusion coefficients of  $\text{Na}^+$ ,  $\text{CO}_3^{2-}$  and  $\text{Cl}^-$  ions are  $10^{-12} \text{ m}^2/\text{s}$ .

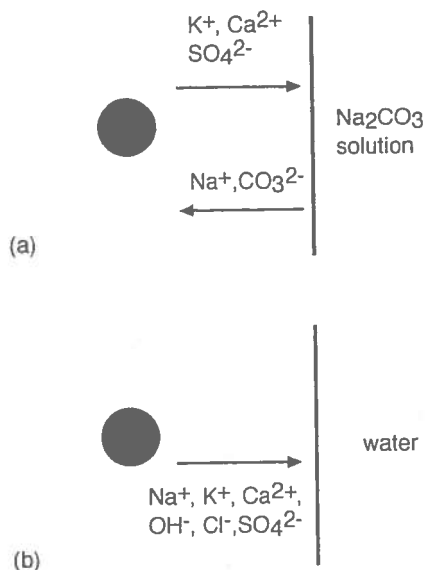


Fig. 2 Diffusion processes in (a) re-alkalisation and (b) desalination.

From the form of the error function, the steady state concentration is reached at  $C_x/C_s = 1.0$  when  $\{x/2 (D_a t)^{1/2}\} = 0$ , i.e. when  $t$  is infinite. Taking instead the value  $C_x/C_s = 0.9$  it is possible to estimate the time,  $t_{90}$ , taken for the concentration  $C_x$  to change 90% of the way from the initial value to the steady state value. For re-alkalisation this represents an increase in sodium and carbonate concentration around the steel from zero to 90% of that of the external electrolyte. For desalination it represents a decrease from the initial concentration of chloride around the steel to 10% of that value. From the error function  $C_x/C_s = 0.9$  when  $\{x/2 (D_a t)^{1/2}\} = 0.05$ . Substituting for  $D_a$  and solving for  $t$  indicates that  $t_{90}$  is  $6 \times 10^{10}$  sec. This is such a long time compared to the timescale of the practical treatments that diffusion can therefore be disregarded as an effective contributor to re-alkalisation or desalination.

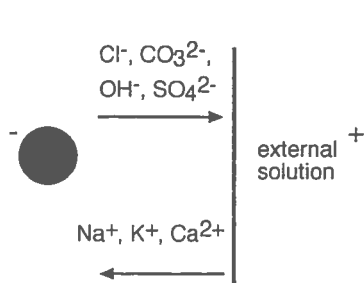
## ELECTROMIGRATION

### Transport numbers

Concrete is an ionic conductor and current flows as a result of the movement of ions. Fig. 3 summarises the various migration processes which can be expected in concrete subjected to an applied electric field. In an electrochemical treatment all negatively charged ions will migrate towards the external anode and all positively charged ions will migrate towards the cathode, the reinforcement. The ions participate in this migration in relative proportions indicated by their respective transport or transference numbers. The transport number  $t_j$  of a particular ion moving in response to an applied electric field is that proportion of the total current  $I$  which is carried by the ion in question and is governed by the mobility of the ion. This is defined as the velocity with which the ion moves through an infinitely dilute solution and can be measured conveniently as the ionic conductivity  $(\lambda_0)_j$  at infinite dilution, values of which are shown in Table 1.

$$t_j = i_j/I = z_j c_j \lambda_j / \sum z c \lambda = \lambda_j / \Lambda \quad [11]$$

$\Lambda$  is the total ionic conductivity of the solution,  $z_j$  is the number of charges borne by species  $j$  which is present in the electrolyte at concentration  $c_j$ . The ionic conductivities of  $H^+$  and  $OH^-$  ions (Table 1) are considerably higher than those of the



other ions because the special structural relationship these ions have with water molecules in solution means that current flow does not need the ions themselves to move. Charges can be passed as bonds break and reform, which is a much faster process and the measured mobility and conductivity are much higher. As temperature is reduced to approach 4°C ( $\lambda_0$ )<sub>OH</sub> and ( $\lambda_0$ )<sub>H</sub> increase considerably because of structural changes in the water, whereas the other values are unchanged.

Fig. 3 Electromigration processes.

Table 1 Values of the ionic conductivity of various ions at infinite dilution and 25°C.  
(units ohm<sup>-1</sup>cm<sup>-2</sup>eq<sup>-1</sup> or 10<sup>-4</sup> ohm<sup>-1</sup>m<sup>-2</sup>eq<sup>-1</sup>)

Ion	H <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>		
( $\lambda_0$ ) <sub>+</sub>	349	50.1	73.5	59.5		
Ion	OH <sup>-</sup>	Cl <sup>-</sup>	1/2SO <sub>4</sub> <sup>2-</sup>	1/2CO <sub>3</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	
( $\lambda_0$ ) <sub>-</sub>	198	75.2	79.8	69.3	44.5	

The values in Table 1 change slightly with increasing concentration, but, as an approximation, the data suggest that the transport numbers in a mixed solution of 0.5 mol/litre sodium hydroxide and 0.5 mol/litre sodium chloride at 25°C are  $t_{Na} = 0.27$ ,  $t_{OH} = 0.53$  and  $t_{Cl} = 0.20$ . Thus 72% of the total current flowing towards the anode results from electromigration of OH<sup>-</sup> and only 28% results from the electromigration of Cl<sup>-</sup>. This principle is universally applicable and in concrete the movement of ions in response to the current passing depends entirely on the mobilities and concentrations of the various ions dissolved in the pore solution.

The implications of this behaviour for desalination are that only a comparatively small proportion of the total current and the total charge passed during the treatment is used in removing chloride from the concrete. Instead of 1 mol (35.5g) of Cl<sup>-</sup> being removed by the passage of 1 Faraday (96500 coulombs) of charge, in one series of the SHRP programme trials [6] 110-125g of Cl<sup>-</sup> was removed by passing 1208 Ah, i.e. 3.1-3.5 mol of Cl<sup>-</sup> was removed by  $4.35 \times 10^6$  coulombs, which is an electrical efficiency of 6.9-7.8%. This low electrical efficiency is a result of the current carried by other negatively charged ions (OH<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) and the heat generated by the current passing through the resistive concrete. It is not inconsistent with the chloride transport number of 0.20 calculated for equimolar sodium hydroxide/sodium chloride solution. Note that this electrical efficiency is different from the chloride removal efficiency reported in the SHRP trials. The latter represents the actual chloride removed as a percentage of the total amount present initially and SHRP reports values up to 55% and the chloride removal efficiencies accepted in industrial practice and confirmed in laboratory studies are up to 50% [3]. This SHRP chloride removal efficiency reflects the amount of chloride bound in the concrete.



This discussion has taken no account of the possibility that at concentrations above about 0.1 mol/litre even "strong" electrolytes like sodium chloride are not completely ionised and exist instead as ion pairs bearing no overall charge. Combined with the possibility that ions may exist as higher order assemblages (triplets, quadruplets etc), this means that the effective equivalent conductance in concrete pore solution may be lower than indicated above. A full analysis would have to consider the contribution of all possible combinations of ions, whether single, pairs or assemblages.

### Speed of electromigration

The general equation for transport processes in solution is the Nernst-Planck equation

$$-J_j(x) = D_j \frac{dC_j(x)}{dx} + z_j F / RT D_j C_j \frac{dE}{dx} + C_j V(x) \quad [12]$$

where the first term on the right is the contribution due to diffusion, the second is due to electromigration and the third is due to convection. As already established, the contribution of diffusion is negligible and it can be assumed that there is no temperature gradient to cause convection. Therefore only the second term need be considered in which  $F$  is 96500 coulombs/equivalent,  $R$  is the universal gas constant (8.3 Joule/deg mol) and  $T$  the absolute temperature (293 K). Equation 12 may be used to calculate the ion flux  $J_j$  and hence how long it would take for chloride ions to be removed in a typical treatment. Assume that an electric field,  $E$ , of 20 volts is applied between a reinforcing bar 50mm below the surface ( $x=0.05$ ) and the external solution, the internal electrolyte contains 0.2 mol/litre of chloride ion ( $C_{Cl} = 0.2$ ) and the diffusion coefficient  $D_{Cl}$  is  $10^{-12} \text{ m}^2/\text{s}$ .

From equation 12  $J_{Cl}$  is  $3.2 \times 10^{-6} \text{ mol/s m}^2$ , which is equivalent to 0.28 mol/m<sup>2</sup> per day and 14 mol/m<sup>2</sup> in 50 days of desalination treatment. However, as noted above, the chloride ion transport number is about 0.2 so that only 2.8 mol/m<sup>2</sup> of chloride will pass in 50 days. Now 1m<sup>2</sup> of concrete 50mm thick might contain 0.15kg (4.2 mol) of chloride ion (1% Cl<sup>-</sup>/cement). Therefore the Nernst-Planck equation indicates that about two thirds of the total chloride will pass out of the concrete into the external solution during the course of a typical desalination treatment. At lower temperatures where the chloride transport number is lower, less chloride will pass out of the concrete. Considering the crudity of this model this broad agreement between the calculated chloride removal rates and those observed in practice (1.5% Cl<sup>-</sup> removed in 8 weeks [3] and 3.1-3.5 mol of Cl<sup>-</sup> removed by 1208 Ah [6]) is encouraging. It suggests that electromigration is the dominant mechanism controlling the desalination process.

### Implications of electromigration in electrochemical treatments

While electromigration of chloride ion is beneficial there are other implications of the balancing electromigration of sodium and potassium ions towards the cathode. These cations have small ionic radius and therefore migrate heavily solvated, i.e. with a sheath of water molecules. This explains the anomalously low diffusion coefficients for these ions reported by Goto and Roy [7], but also suggests why water may concentrate at the cathode, as is sometimes noticed in cathodic protection and desalination. On the other hand, water can be electrolytically reduced at the cathode (equation 8) in which case the steel becomes dry. It seems likely that the balance between electromigration and reduction of water governs whether the steel appears wet or dry at the end of the treatment.

A more serious consequence of electromigration and electrolysis is that the higher pH around the reinforcement and the artificially high concentration of sodium and potassium ions may promote alkali-aggregate reaction in potentially sensitive aggregates. This will be exacerbated by the wet conditions resulting from the movement of water. On the other hand, the hydroxyl ions produced at the reinforcement electromigrate through the concrete. The hydroxyl ion transport number suggests that its speed of electromigration could be four or more times that of chloride ion. In principle, hydroxyl could be driven out of the concrete altogether.

Finally, electromigration cannot account for the observed penetration of carbonate ions during re-alkalisation, since negatively charged ions are driven out of the concrete towards the external electrode.

## ABSORPTION

Another diffusion mechanism can operate in re-alkalisation but not desalination: simple absorption. If the concrete to be treated is not saturated, it will absorb sodium carbonate solution from outside. Once again, the time to reach equilibrium may be calculated but the range of starting conditions is so wide that it is hard to choose typical conditions. If absorption is strong (as in dry concrete) a layer 50mm deep can be saturated in 24 hours whereas if absorption is weak (damp, partially saturated concrete) it will not be saturated even after 10 days and experience confirms that it takes weeks for good, dense concrete to saturate by absorption. Polder [8] found that alkalinity penetrated only 2-5 mm in 8 days treatment of cores with molar sodium carbonate solution. However, considering that the sort of concrete which is likely to need to be re-alkalised is of poor quality and therefore highly absorbent, simple absorption of sodium carbonate solution could make a major contribution.

## ELECTRO-OSMOSIS

### Origin of the effect

Electro-osmosis is one of several electrokinetic effects well established in colloid science. Particles in contact with electrolyte acquire a surface charge because the relative affinities of cations and anions for the solid and the solution are different. A charged particle is surrounded by counterions (of opposite charge) to form a diffuse electrical double layer whose extent depends on the electrolyte concentration: increasing concentration compresses the layer closer to the particle from 100 nm at  $10^{-5}$  mol/litre to 1 nm at 0.1 mol/litre of singly charged ions. The existence of the charge on colloidal particles is confirmed by their movement in response to an applied electric field (electrophoresis). Electro-osmosis is the inverse of electrophoresis, in that a stationary porous plug of particles is formed and the liquid in the centre of the pores beyond the double layer moves in the opposite direction in response to the electric field. The network of fine capillaries in concrete is lined with particles of colloidal size carrying an electric charge which is balanced by the envelope of counterions in the pore solution. In this case the zeta potential is the potential at the shear plane between the stationary envelope and the moving stream of solution. The fluid velocity in a porous plug rises from zero within the double layer to  $v_e$  in the body of the pore and provided the pore is large compared to the thickness of the electrical double layer then the flow velocity (but not the volumetric flow rate) is independent of the size and number of the pores.

## Applications in concrete

The typical pore size in concrete is  $10^{-6}$  m, so the double layer must be less than  $10^{-8}$  m (10 nm) thick for the flow rate to be independent of size and number of pores. This will be so when the electrolyte solution is more concentrated than  $10^{-3}$  mol/litre. Literature values for the concentration of ions in concrete pore solutions are about 0.2 mol/litre (e.g. ref. 9) so this condition holds true, but there seem to be no data available for the pore solution composition in carbonated concrete and lower ionic concentrations are likely here.

In these circumstances, the electro-osmotic velocity is given by [10]:

$$v_e = - \frac{D\zeta E}{\eta} \quad [14]$$

where  $D$  and  $\eta$  are the permittivity and viscosity of the liquid,  $E$  the electrical field strength and  $\zeta$  the zeta potential. Taking  $D$  to be  $695 \times 10^{-12}$  Faraday/m and  $\eta$  to be  $10^{-3}$  N/m.s it is possible to estimate  $v_e$  from  $\zeta$ . Reported values for the zeta potential of young cement particles in water range from -10 to -30 mV [11,12]. The negative sign predicts that electro-osmotic flow of liquid will take place from the external solution towards the cathode, as is observed in practice. Therefore, in a typical concrete with a 50 mm depth of cover over the steel and a treatment voltage of 20 V, electric field strength is 400 V/m. Substituting these values into equation 14 gives a range of  $v_e$  between  $2.8 \times 10^{-6}$  and  $8.3 \times 10^{-6}$  m/s. These values suggest that it would take electrolyte solution between  $2 \times 10^4$  and  $6 \times 10^4$  sec to penetrate 50mm into concrete during a re-alkalisation treatment. This rate of penetration is somewhat faster than observed in practice but more important is the fact that it is significantly higher than what can be achieved by simple diffusion or absorption and adds weight to the suggestion that electro-osmosis could be the dominant mechanism in re-alkalisation. The main uncertainty in this calculation is the zeta potential which may be different in mature hydrated cement and for calcium carbonate.

Implications of the electro-osmosis mechanism are that the flow velocity is independent of the pore size of the concrete and of the composition of the penetrating liquid, provided that the latter has a sufficiently high electrolyte concentration to keep the double layer compressed. Penetration should occur equally well for uni- or multi-valent electrolytes and the movement of solution into the concrete towards the steel should result in a significant increase in the moisture content of the internal concrete.

Some of these features have been confirmed in practice. For example, Miller and Nustad [13] reported that a black layer of a greasy consistency was formed around the steel but did not identify it. The black colouration may be due to the formation of FeO (black magnetite), but the greasy consistency is probably due to the high moisture content of the concrete. However, of a selection of electrolytes studied in preliminary experiments [14] only sodium carbonate solution penetrated the concrete from outside. Sodium chloride, sodium nitrite, and calcium hydroxide were all ineffective, perhaps due to specific interactions between the electrolytes and concrete.

Hydroxyl ion is also produced at the cathode and electromigrates away from it. Since the electro-osmotic velocity is considerably higher than, and in the opposite direction to, the electromigration, the spreading of hydroxyl from the reinforcement would be suppressed by electro-osmosis. Therefore the zone of alkalinity around the steel would probably be smaller in re-alkalisation than in desalination.

Another uncertainty about this analysis is the fact that the surfaces lining concrete pores are carbonated. Indeed, according to Nustad [15] re-alkalisation works in carbonated concrete but not in uncarbonated. The differences between the two cases are likely to result from the different zeta potentials in carbonated and uncarbonated concrete. Also carbonation coats pores making them smaller. Either of the factors will change the parameters in equation 14, but work is needed to establish their effects.

## CONCLUSION

Re-alkalisation and desalination are successful treatments for concrete but the mechanisms by which sodium carbonate penetrates the concrete and chloride ions are removed are not firmly established. Much more work is needed to elucidate them so that treatment conditions can be optimised through a sound theoretical basis. Simple concentration-gradient-controlled diffusion of the species through concrete is too slow to make a significant contribution. Electromigration is probably the main contributor in desalination but chloride removal efficiencies expressed in terms of the total charge passed may be less than 10% due to the presence of other charged ions and the heating effect of the current. Electromigration prevents sodium carbonate penetration in re-alkalisation and a combination of electro-osmosis and direct absorption are probably the main contributors here. However, this cannot explain why other electrolytes are ineffective.

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